Recovery of Metals from Oxidised Metalliferous Materials

TECHNICAL FIELD

5   A process for the recovery of metals from oxidised metalliferous materials is disclosed. The term "oxidised metalliferous material" includes lateritic materials, electric arc furnace (EAF) dusts & residues, electrolytic zinc plant residues, zinc oxides and zinc ferrites,

10   goethite, arsenic trioxide, etc. The lateritic materials are typically laterite ores, such as nickel, cobalt and optionally other metal laterites.

BACKGROUND ART

15   Oxidised metalliferous materials such as laterites can have a refractory characteristic. For this reason smelting processes have been used to recover metals such as nickel and cobalt from such materials. However, the severe environmental repercussions of smelting processes

20   have lead to the development of hydrometallurgical recovery processes for some oxidised metalliferous materials.

Known hydrometallurgical processes for the recovery of metals such as nickel and/or cobalt from laterite ores

25   have primarily involved pressure acid leaching, typically at high pressures and employing sulfuric acid. Sulfuric acid is employed because of its abundance, cost and well-known chemistry. US 6,261,527 does discloses a hydrometallurgical process for the recovery of nickel

30   and/or cobalt from laterite ores involving atmospheric pressures, however, it still employs sulfuric acid leaching.

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Recently, a process has been proposed which is based on a chloride acid leach as opposed to a sulphuric acid leach. Whilst a chloride leaching medium is a powerful lixiviant, it is corrosive and requires apparatus to be
5   chloride resistant. Chloride media have also been avoided because they have a high acid consumption and can present difficulties with the control of iron and magnesium leaching, both metals typically present in laterites.

The company Chesbar Resources (now known as Jaguar
10   Nickel Inc.) presented a paper at the ALTA 2002 Conference (Nickel/Cobalt-9 session) in Perth, Western Australia on May 18-20, 2003. The paper entitled "Beyond PAL: The Chesbar Option, AAL" outlined a process for the atmospheric chloride acid leaching of nickel laterite
15   ores. The process is now disclosed in WO 2004/101833.

The Chesbar process requires the use of a pyrohydrolysis stage to regenerate from the process liquor HCl as a gas for recycle to leaching, and to regenerate magnesium oxide for use in a nickel/cobalt precipitation
20   stage. However, HCl gas is difficult to handle, being highly corrosive. In addition, a pyrohydrolysis stage is endothermic, requiring the input of significant energy, and hence has both high capital and operating costs.

It would be advantageous if a halide based process
25   could be provided for the recovery from oxidised metalliferous materials of metals such as nickel, cobalt, copper, precious metals, magnesium etc, which does not require a pyrohydrolysis stage and which does not require recycle of a corrosive gas for the acid leaching stage.

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SUMMARY OF THE DISCLOSURE

In a first aspect there is provided a process for recovering a target metal from an oxidised metalliferous material, the process comprising the steps of:

5   - in a leaching stage, leaching the oxidised metalliferous material with an acidic aqueous halide solution to leach the target metal into solution, the leaching solution being generated by adding sulfuric acid to a solution comprising a metal halide;

10   - passing the solution from the leaching stage to a target metal recovery stage in which the target metal is recovered from the solution whilst the metal halide is retained in solution; and

- returning the solution with the metal halide therein

15   from the target metal recovery stage to the leaching stage.

The process thus generates an acidic aqueous halide solution, rather than employing sulfuric acid leaching. The resultant halide based leaching process is typically

20   operated at atmospheric pressures. Whilst elevated leaching pressures can be employed (eg. using autoclave leaching) this will depend on the oxidised metalliferous material to be leached and whether more rapid target metal extraction is required.

25   Further, the addition of sulfuric acid to generate the acidic aqueous halide solution is exothermic and hence allows the pyrohydrolysis stage of the prior art to be eliminated. This part of the process also avoids the recycling of hydrogen chloride gas as per the prior art.

30   Thus, sulfuric acid addition and acidic aqueous halide solution generation can provide substantial savings in capital and operating costs, typically well in excess of the cost of producing sulfuric acid.

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However, in applications such as the treatment of electrolytic zinc plant residues, sulfuric acid is a by-product of the electrolytic zinc plant process, so the acid can then be utilised economically in the process for
5   treatment of such residues.

Where a sulfuric acid plant is employed to produce the sulfuric acid for addition to the present process, such plants produce massive amounts of excess heat (ie. as a result of exothermic reactions) which can then be used
10   to heat the process solution, to provide further savings in capital and operating costs.

Depending on the oxidised metalliferous material to be treated, the target metal can include nickel, cobalt, zinc, copper, arsenic, iron, magnesium, precious metals
15   such as gold, silver, platinum etc.

Usually the metal selected for the metal halide solution is one that does not interfere with leaching of the target metal or its recovery as a precipitate. A metal may be selected that forms a precipitate with the sulfate
20   anion of the acid such that, with the generation of the leaching solution, a hydrohalous acid forms together with a precipitate of the metal sulfate. In this regard, the metal may be calcium so that the metal sulfate precipitate is calcium sulfate, which can then form a saleable by-
25   product. However, sodium can be present as a solution metal where the halide is derived from a sodium halide salt. In addition, magnesium chloride may also be used when the material contains high levels of magnesium (eg. to suppress Mg extraction).
30   Usually and expediently the halide of the metal halide solution is chloride, again because of the abundance of low cost chloride salts such as NaCl. Hence, hydrochloric acid will continuously be formed as the

solution metal precipitates with the sulfate, without the
need to form and add or recycle hydrogen chloride gas, as
in the prior art. This avoids the handling difficulties
and hazards associated with hydrogen chloride gas.

5   However, other halides such as bromide or iodide can be
employed, for example, where the metalliferous material
includes precious metals. In this regard NaBr may then
also be added to the solution, as bromide complexes more
strongly than chloride and hence can stabilise the

10   precious metals in solution.

        Depending on the type of oxidised metalliferous
material, the leaching stage may comprise first and second
leaching stages that operate in a counter-current
configuration, whereby:

15   - the oxidised metalliferous material is added to the
first leaching stage to contact the solution and leach
target metal into solution; and
        - the solution from the first leaching stage is separated
from first leached solids and passed to the target metal

20   recovery stage; and
        - the first leached solids are passed to the second
leaching stage to be mixed with the leaching solution; and
        - the solution from the second leaching stage is separated
from second leached solids and passed to the first

25   leaching stage, and the second leached solids are
discarded as residue.

        By employing a two-stage leaching process, target
metal(s) can be partially leached from the oxidised
metalliferous material in the first leaching stage, and

30   can be further leached into solution in the second
leaching stage by contacting the first solids with the
hydrohalous acid. Then, leached target metal(s) from the
second leaching stage can be returned with the solution to

the first leaching stage, and thereafter can pass with the
separated solution from the first leaching stage to the
target metal recovery stage.

Further, when the solids from the first leaching
5   stage are passed to the second leaching stage they are, in
effect, contacted with a solution of relatively high
acidity (ie. compared to the solution acidity in the first
leaching stage) such that a proportion of remaining target
metal in the solids is then leached into the solution for
10   subsequent recovery.

In one form the leaching solution can be generated in
a separate hydrohalous acid generation stage in which the
sulfuric acid is added to the solution comprising the
metal halide, and this leaching solution is then fed to
15   the second leaching stage to mix with the first leached
solids. This stage allows for a metal sulfate precipitate
to be formed and easily separated out from the leaching
solution, which metal sulfate may be of a relative high
purity. For example, the metal of the metal halide
20   solution can be one that forms a precipitate with the
sulfate anion of the sulfuric acid such that, with the
generation of the leaching solution, a hydrohalous acid
forms together with a precipitate of the metal sulfate,
the metal sulfate precipitate being removed as a solid
25   residue stream from the hydrohalous acid generation stage
(eg. as a saleable by-product such as calcium sulfate).

In addition, a portion of that solution being passed
from the second to the first leaching stage can be
diverted to the hydrohalous acid generation stage to
30   thereby easily provide the solution comprising the metal
halide, with the balance of leaching solution then being
made up from the solution of the added sulfuric acid.

In another form the sulfuric acid can be added directly to the second leaching stage. Again, the metal of the metal halide solution can be one that forms a precipitate with the sulfate anion of the sulfuric acid such that, with the generation of the leaching solution, a hydrohalous acid forms together with a precipitate of the metal sulfate, the metal sulfate precipitate then being removed with the second leached solids and discarded as residue.

Usually the target metal recovery stage comprises a precipitation stage in which a precipitate of the target metal is formed by adding a precipitation agent to the solution. This is a simple and expedient way of removing the or each target metal. When the oxidised metalliferous material comprises more than one target metal, a respective precipitation stage can thus be provided for each target metal. These stages may be arranged in the process in series.

In addition, whilst an anion of the precipitation agent can cause target metal precipitation, the agent may also be used to introduce the metal of the metal halide solution (eg. the precipitation agent cation may be calcium). Thus, addition of the precipitation agent can maintain a desired concentration of that metal in solution, and to balance the process the metal may later be removed as a metal sulfate precipitate when the hydrohalous acid is formed.

The oxidised metalliferous material may comprise more than one target metal, and a respective precipitation stage is provided for each target metal.

For example, when the oxidised metalliferous material includes iron, a proportion of that iron can be leached into solution in the leaching stage, and at least a

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proportion of the leached iron can then be precipitated in
an iron precipitation stage as ferric oxide through the
addition of calcium carbonate as the precipitation agent.
In such case, the oxidised metalliferous material may be
5   given sufficient residence time in the leaching stage such
that leached iron is oxidised through to haematite.

Further, in the iron precipitation stage the addition
of the calcium carbonate increases the solution pH and
causes the iron to precipitate as ferric oxide.

10   When the target metal includes copper, the precious
metal can be precipitated in a copper precipitation stage
by adding calcium carbonate as the precipitation agent.

When the target metal includes a precious metal, the
precious metal can be precipitated in a precious metal
15   precipitation stage by adding NaSH as the precipitation
agent.

When the target metal includes nickel and/or cobalt,
the nickel and/or cobalt can be precipitated in a
nickel/cobalt precipitation stage by adding calcium
20   hydroxide as the precipitation agent.

When the target metal includes magnesium, the
magnesium can be precipitated in a magnesium precipitation
stage by adding calcium hydroxide as the precipitation
agent.

25   In both of these cases the calcium hydroxide can be
slaked lime.

In an alternative arrangement the target metal
recovery stage can comprise an electrolytic recovery
stage, whereby the solution from the leaching stage is
30   passed to one or more electrolysis cells for metal
recovery by electro-deposition. When the oxidised
metalliferous material comprises more than one target
metal, a respective electrolytic recovery stage can be

provided for each target metal, eg. arranged in series in the process.

For metalliferous material comprising multiple target metals, combinations of precipitation and electrolytic
5 recovery stages in series or parallel arrangements in the process may also be employed.

In a process variation that doesn't employ the separate hydrohalous acid generation stage, and where iron is present in the metalliferous material, air can be added
10 to the first and/or second leaching stages, with or without the addition of copper as a Cu^+/Cu^{2+} oxidation couple, to maximise iron oxidation such that all iron precipitates as ferric oxide (haematite) in the leaching stage.

15 The leached solids and solution from the second leaching stage are usually separated in a separation stage, with the solution being recycled to the first leaching stage and the solids discarded as leach residue.

In one option, solution separated from solids after
20 the or each precipitation stage can be returned directly to the first leaching stage. In an alternative arrangement, solution separated from solids after the or each precipitation stage can be first passed to the separation stage after second leaching to wash the
25 separated solids, and then be recombined with the solution recycled to the first leaching stage. This wash can help maximise retrieval of the target metal.

Usually the oxidised metalliferous material has a residence time in the leaching stage of greater than 10
30 hours, so that metals such as iron are leached and fully oxidised (eg. through to haematite). This ensures that discarded residues when disposed of are in a more stable and safe form for the environment.

The sulfuric acid may be added to the leaching stage
to achieve a pH in the range 0 to 1 and a solution Eh of
600mV (ref Ag/AgCl). The solution in the leaching stage
can have a temperature ranging from 85 – 110°C.

5   When the halide in the metal halide solution is
chloride, total chloride concentration may be in the range
of 6 to 8 M, and when the metal in the metal halide
solution is calcium, at least 30g/l of $CaCl_2$ can be
maintained in the leaching stage.

10   In a second aspect there is provided a process for
leaching a target metal from an oxidised metalliferous
material, the process comprising first and second leaching
stages in which an acidic aqueous halide solution
generated from sulfuric acid and used for leaching the
15 target metal into solution passes counter-currently
therethrough, wherein the acid generated from sulfuric
acid is added to the second stage, and the oxidised
metalliferous material is fed to the first leaching stage
and contacted with a recycle of residual acid in solution
20 from the second leaching stage to leach the material and
produce first leached solids, and wherein the solution is
separated from the first leached solids and may be passed
to target metal recovery, whereas the first leached solids
are passed to the second leaching stage for contact with
25 the added acid for further leaching of the solids whilst
producing the residual acid recycle solution.

        The acid generated from sulfuric acid can be
generated in a separate stage from the second leaching
stage prior to being added thereto, or may be generated in
30 the second leaching stage.

        The process of the second aspect finds particular
application where the oxidised metalliferous material
includes iron, particularly at high levels. Thus a

proportion of the iron can be leached into solution in the first leaching stage and a proportion of the leached iron can later be removed (eg. precipitated as ferric oxide, typically haematite). The ferric oxide (eg haematite) precipitate can for example pass with the solids to the second leaching stage, to thereafter pass with leaching residue from the second leaching stage to disposal.

The process of the second aspect can otherwise be as defined for the first aspect.

This disclosure also extends to any metal produced by the process of the first and second aspects.

BRIEF DESCRIPTION OF THE DRAWINGS

Notwithstanding any other forms which may fall within the scope of the process as defined in the Summary, specific forms of the process will now be described, by way of example only, with reference to the accompanying drawing in which:

Figure 1 shows a flow diagram for a first process for recovering metals from a laterite ore;

Figure 2 shows a flow diagram for a second process for recovering metals from a laterite ore; and

Figure 3 is an X-ray diffraction plot for a bassanite precipitate.

DETAILED DESCRIPTION OF SPECIFIC EMBODIMENTS

Process of Figure 1

Figure 1 depicts a first recovery process for a lateritic ore and comprises a LEACH process coupled to a PURIFICATION (eg. precipitation) process, together with solution recycle. The recovery process of Figure 1 can be generalised to the recovery of one or more target metals from other oxidised metalliferous materials.

In the LEACH process, a lateritic ore 10 (which can also be a pre-prepared laterite concentrate) is crushed and ground at 12 and is then fed to an optional two stage counter-current leaching process having a first leach

5   stage 14 and a second leach stage 16, both of which operate at atmospheric pressure. The counter-current two stage leach benefits H_2SO_4 consumption as compared to a single stage leach but is more complex. In addition, either leach stage has the option of being run at higher

10   pressures (and thus higher temperatures) using an autoclave (eg. to minimise H_2SO_4 consumption and increase target metal extraction efficiencies, although increasing capital and operating costs).

Whilst a single stage leach can be used for

15   simplicity and cost, the actual configuration used depends on the metalliferous material feed composition. With feed variation, the degree of benefit of H_2SO_4 consumption will vary and the two stage configuration may or may not be required.

20   An acidic aqueous calcium chloride solution is passed through leach stage 16, the solution having a pH in the range of 0-1. This pH is achieved through the addition of sulfuric acid at levels sufficient to leach into solution target metals such as nickel, cobalt and precious metals.

25   The solution leaches the already partially leached laterite residual solids that are received from leach stage 14 via a thickening stage 18.

In leach stage 16 the solution has a temperature in the range of 85 to 110°C, an Eh controlled at ~600mV

30   (versus Ag/AgCl), and a total chloride concentration in the range of 6 to 8M. However, the required solution for leaching depends on the mineralogy of the metalliferous material, in particular the types and quantities of acid

consumers contained in the ore. For example, for lateritic ores, a minimum of 30g/l of $CaCl_2$ is maintained in the leach to suppress jarosite formation, in turn optimising iron precipitation as haematite. The solution residence
5   time is typically greater than 10 hours, to achieve full iron oxidation, and to release target metals into solution.

Optionally, air can be sparged into the solution to maximise iron conversion through to haematite, and copper
10   can be added to further assist oxidation as described below.

When higher leach solution temperatures are required (eg. up to and in the vicinity of 200°C) then leaching in an autoclave can be employed.
15   The slurry of leached solids and solution is then passed from stage 16 to a filtration stage 20 where residual solids are filtered and separated, the solids being washed by a $CaCl_2$ recycle stream 22 from the PURIFICATION process (with an optional additional water
20   wash being employed) to recover interstitial target metals. The washed solids are disposed of whereas the solution and stream 22 (and any wash water) are combined and recycled to the first leach stage 14.

The acid depleted recycle now has a higher pH (the
25   differential may be 1 or greater) and is used for a preliminary leach of the ore 10. The acid depleted recycle typically leaches a proportion of the iron into solution, from goethite (α-FeOOH) and akagenite (β-FeOOH) through to haematite (Fe_2O_3) as described below. Again the residence
30   time can be 10 hours or greater and, aside from pH and Eh, the solution parameters in stage 14 are similar to stage 16 described above. The partially leached solids and solution are then passed to thickening stage 18 where a

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clear liquor overflow is passed to the PURIFICATION
process and the solids underflow is passed to second leach
stage 16.

    In the PURIFICATION process the clear liquor overflow
5   is first passed to an iron removal stage 24, where calcium
carbonate is added to cause haematite (Fe_2O_3) to form and
precipitate (described below). The haematite is filtered
out at separation stage 26.

    Optionally, where copper has been used in the
10 leaching process to enhance oxidation, the copper is next
removed from the liquor at copper precipitation stage 28
by the addition of calcium carbonate, and is filtered out
at separation stage 30. The copper residue can be
reclaimed, or recycled back to the leaching process for
15 re-use, as recycle 32.

    The liquor is now passed to a precious metal recovery
stage 34 where NaSH is added to precipitate out the
precious metals (described below). The precious metals are
filtered out at separation stage 36 and recovered by
20 smelting etc.

    Next, the liquor is passed to a nickel/cobalt
recovery stage 38 where slaked lime ($Ca(OH)_2$)is added to
precipitate out the nickel and cobalt. The nickel and
cobalt are filtered out at separation stage 40 and are
25 then recovered. Any lead (Pb) in the ore can also be
recovered at this stage.

    Finally, where magnesium is present in the ore the
liquor can be passed to a magnesium recovery stage 42,
again where slaked lime ($Ca(OH)_2$) is added to precipitate
30 out the magnesium (described below). The magnesium is then
filtered out at separation stage 44 and recovered,
optionally with any other metals still present in the
liquor.

The resulting purified liquor (CaCl$_2$ recycle solution 22) is now returned to the LEACHING process.

Process of Figure 2

Figure 2 depicts a second alternative recovery process, where like reference numerals are used to denote similar or like process stages to those of Figure 1. The recovery process of Figure 2 is again depicted for a laterite feed but can be generalised to the recovery of one or more target metals from other oxidised metalliferous materials.

The recovery process of Figure 2 again comprises a two-stage leach process, with separated solution from the first leaching stage again being passed to target metal recovery stages (eg. precipitation and/or electrolytic recovery), but with solution recycle from the target metal recovery stages direct to the first leaching stage.

In the two-stage leach process, a crushed and ground laterite feed 10 (having the metal concentration listed) is fed to the first leach stage 14 and then to second leach stage 16, both of which again operate at atmospheric pressure. Again, either leach stage has the option of being run at higher pressures (and temperatures) using an autoclave.

As distinct from the process of Figure 1, the process of Figure 2 comprises a separate acid generation stage 17 in which the acidic chloride solution is generated. In this regard, an H$_2$SO$_4$ solution is added to stage 17 together with a diverted stream 19, being a portion of the leach recycle ("stream 9"). The stream 9 comprises aqueous calcium chloride so that the diverted stream 19, which when contacted with the H$_2$SO$_4$ solution, generates the acidic chloride (HCl) solution and a calcium sulfate

precipitate (separated in stage 17 as a saleable by-product).

The acidic chloride (HCl) solution is passed to leach stage 16, the solution having a pH in the range of 0-1, sufficient to leach into solution target metals such as nickel, cobalt, iron, magnesium, precious metals etc. The acidic solution leaches the partially leached residual solids ("stream 8") that are received from leach stage 14 via solid/liquid separation stage 18.

In leach stage 16 the solution has a temperature in the range of 85 up to 110°C, with other parameters being similar to those described for the process of Figure 1.

The slurry of leached solids and solution is then passed from stage 16 to another solid/liquid separation stage 20, where residual solids are separated and discarded whereas part of the solution ("stream 5") is recycled to the first leach stage 14.

Again, this acid depleted recycle typically leaches a proportion of any iron in the feed into solution, with the solution parameters in stage 14 being similar to those described for the process of Figure 1.

The partially leached solids and solution are passed to solid/liquid separation stage 18 (as "stream 7") where a clear liquor overflow ("stream 6") is passed to the target metal recovery, the solids underflow ("stream 8") being passed to second leach stage 16.

In target metal recovery the clear liquor overflow is first passed to an iron precipitation stage 24, where calcium carbonate is added to cause haematite (Fe_2O_3) to form and precipitate. The haematite is separated out (eg. filtered) at separation stage 26.

A portion of the liquor ("stream 3") is recycled to the first leach stage 14, with the balance being passed to

a nickel/cobalt removal stage 38. In stage 38 slaked lime
(Ca(OH)$_2$) is added to precipitate out the nickel and
cobalt, which are then separated out (eg. filtered) at
separation stage 40, for subsequent recovery.

5   A portion of the liquor ("stream 2") is again
recycled to the first leach stage 14 whereas, to separate
out magnesium present in the feed, the balance of liquor
is passed to a magnesium removal stage 42. In stage 42
again slaked lime (Ca(OH)$_2$) is added to precipitate out the

10   magnesium. The magnesium is then separated out (eg.
filtered) at separation stage 44, for subsequent recovery.
The separated liquor from stage 44 ("stream 1") is
recycled to the first leach stage 14, (combining with
streams 2 and 3 as stream 4).

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Examples

      Non-limiting examples of the processes described
above will now be provided.

20   **Example 1**

      A first process, hereafter referred to as the Intec
Oxidised Metalliferous Materials Process (IOMMP) was
developed as a halide-based alternative for the recovery
of nickel and associated by-products from lateritic

25   deposits. Previously the development of such deposits was
generally by way of pressure acid leach (PAL) or high
pressure acid leaching (HPAL).

      The IOMMP employed a chloride medium, as opposed to
the conventional sulphate medium in PAL and HPAL. The main

30   advantage of the chloride medium is the ability to operate
the leach at atmospheric pressure, without reliance on
pyrohydrolysis to recover HCl for leaching and MgO for
liquor purification.

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The IOMMP was based on the input of H_2SO_4 for leaching and a calcium based alkali for purification, which eliminated the need for pyrohydrolysis. The IOMMP process was also not constrained by the types of halide
5   salts employed. In this respect NaCl was a more cost effective source of chloride ion, whilst NaBr was able to be used to enhance the complexing of precious metals (Au, Ag, Pt, etc).

Conditions in the IOMMP leach were conducive to
10   haematite precipitation. In particular, the temperature was in the range of 85 to 110°C, pH 0-1, residence time >10hours, Eh was controlled at ~600mV (versus Ag/AgCl), and total chloride was in the range of 6 to 8M.

Chemistry
15   Reference will now be made to the two main circuits of leaching and target metal recovery of Figures 1 and 2.

Leaching

The leach configuration and conditions depended on:

- the mineralogy of the feed material; and
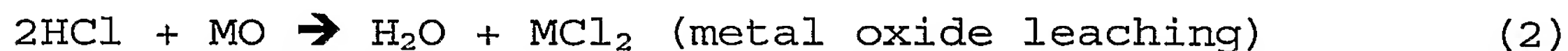20   - the relationship between acid consumption and metal extraction.

The counter-current two stage leach of Figures 1 and 2 was observed to benefit H_2SO_4 consumption as compared to a single stage leach.
25   The solution for leaching depended on the mineralogy of the material, in particular the types and quantities of contained acid consumers. A minimum of 30g/l of $CaCl_2$ was maintained in the leach to suppress jarosite formation, in turn optimising iron precipitation as haematite.
30   The preferred source of chloride was NaCl due to its low cost, but when the feed material contained high levels of Mg, then $MgCl_2$ was used to suppress Mg extraction in order to minimise H_2SO_4 demand. The actual H_2SO_4 demand was

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a compromise between its cost and the value of extracted metals.

The level of $CaCl_2$ in the incoming leach liquor was equivalent to the H_2SO_4 demand according to the following mechanism:

H_2SO_4 + $CaCl_2$ → $CaSO_4$ + 2HCl (acid addition to leach) (1)

2HCl + MO → H_2O + MCl_2 (metal oxide leaching)   (2)

MCl_2 + CaO → $CaCl_2$ + MO (purification)   (3)

Thus the higher the overall metal leached the greater was the background of $CaCl_2$, due to the increased addition of acid to the leach and alkali in purification.

The option existed to add NaBr to the background solution where high levels of precious metals existed in the feed. Bromide was observed to be a stronger complex than chloride in terms of its ability to stabilise the precious metal ions in solution.
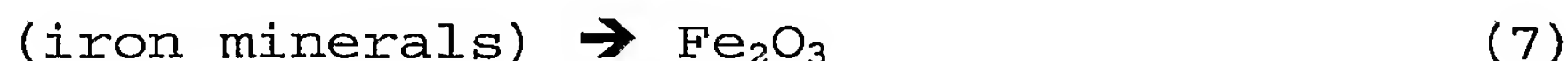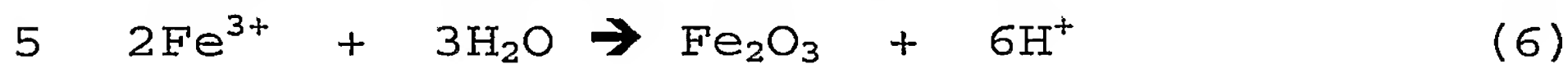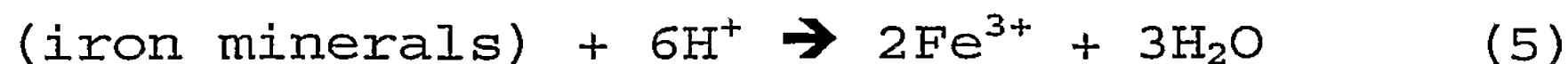
An important aspect of the leach was to maximise the rejection of iron as haematite (Fe_2O_3). The formation of goethite (α-FeOOH) and akagenite (β-FeOOH) in the chloride medium was noted, and over time the FeOOH underwent dehydration to haematite according to the reaction:

2FeOOH → Fe_2O_3 + H_2O (4)

Haematite was the main form of iron oxide generated and this was attributed to the high residence time at > 10 hours, the relatively high temperature at >85°C, the desiccating effect of the chloride medium and the availability of seed particles in the continuous leach.

Another important aspect of the process was to minimize the consumption of H_2SO_4 and consequently $CaCO_4$. This was achieved through the dehydration reaction (4) described above. Haematite (Fe_2O_3) was a significantly more stable form of iron oxide than goethite or the various forms found in laterite and other feed materials.

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The transformation of iron minerals through goethite to haematite showed no net consumption of acid as demonstrated by the reactions below:

$$\text{(iron minerals)} + 6H^+ \rightarrow 2Fe^{3+} + 3H_2O \qquad (5)$$

$$2Fe^{3+} + 3H_2O \rightarrow Fe_2O_3 + 6H^+ \qquad (6)$$

$$\text{(iron minerals)} \rightarrow Fe_2O_3 \qquad (7)$$

Acid consumption was very significantly reduced by this route, and consequently, process economics were significantly improved.

Air was able to be added to the leach to maximise iron precipitation by ensuring any reduced species such as FeO were oxidised to Fe_2O_3 as per the reaction:

$$4FeO + O_2 \rightarrow 2Fe_2O_3 \qquad (8)$$

The rate of air addition was controlled to maintain the Eh at ~600mV (versus Ag/AgCl). Further a possibility existed for the addition of copper into the solution, as the Cu^+/Cu^{2+} oxidation couple was more effective than the Fe^{2+}/Fe^{3+} couple in the uptake of oxygen.

The residue generated from the leach is firstly washed with brine from the purification circuit to displace valuable metal ions from the interstitial liquor. Subsequently a countercurrent washing regime is used to minimise wash water, which ultimately must be evaporated from the liquor through the input of heat.

Target Metal Recovery

Metal recovery in Figure 1 was usually based on precipitation using the calcium based alkalis of $CaCO_3$ and $Ca(OH)_2$. An alternative to precipitation was electrolytic recovery or even solvent extraction or ion exchange, where the various metal cations could be extracted in the process, replenishing the solution with acid (H^+). The choice of metal recovery step was a trade-off between the cost of the process step and its increased complexity,

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versus the reduced acid demand and the possibly higher value of products generated.

In the alkali precipitation route iron was the first to be precipitated at pH 2 with the addition of limestone according to the reaction:

$$2Fe^{3+} + 3CaCO_3 \rightarrow Fe_2O_3 + 3CO_2 + 3Ca^{2+} \hspace{2cm} (9)$$
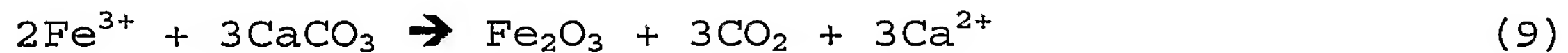
Subsequently, copper (where added or present) was precipitated at pH 3 to 4 with the addition of limestone according to the reaction:

$$4CuCl_2 + 3CaCO_3 + 3H_2O \rightarrow 2Cu_2(OH)_3Cl + 3CO_2 + 3CaCl_2 \hspace{0.5cm} (10)$$
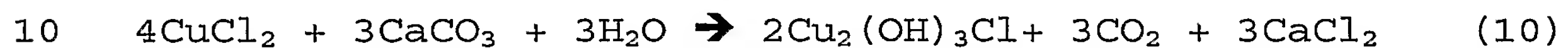
Precious metal extraction where required was via NaSH addition and was followed by precipitation of the remaining base metal ions with slaked lime addition according to the reaction:

$$M^{2+} + Ca(OH)_2 \rightarrow MO + Ca^{2+} + H_2O \hspace{2cm} (11)$$

In the nickel and cobalt removal stage, nickel and cobalt were precipitated by slaked lime addition. In the final removal stage magnesium was precipitated by slaked lime addition according to the reaction:

$$Mg^{2+} + Ca(OH)_2 \rightarrow MgO + Ca^{2+} + H_2O \hspace{2cm} (12)$$
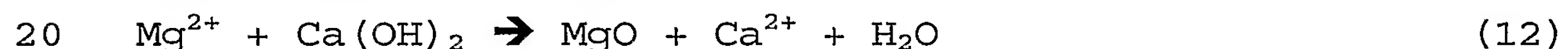
The $CaCl_2$ rich liquor remaining was returned to the leach.

Example 2

Zinc Ferrite Leach Trial

A leach trial was carried out on a sample of zinc ferrite residue from an Electrolytic Zinc Plant to determine metal extraction efficiencies.

A 50kg (wet) sample of the zinc ferrite was slurried at a density of 200 g/L in a brine formulated to match the process conditions for the first leach stage.

The brine had the following major components:

Component	Concentration g/L
$CaCl_2$	280
NaCl	50
$FeCl_3$	50
$ZnCl_2$	75

The solution metal concentrations were monitored over time with the results shown in the table below.

Time (Hours)	[Fe] (g/L)	[Cu] (g/L)	[Pb] (g/L)	[Zn] (g/L)	[Ag] (ppm)	Temp	pH	Dry Weight (kg)
0	20.5	1.0	6.2	36.4	20	105	0.05	46.0
1	21.0	-	-	40.4	-	106	0.30	-
3	21.3	-	-	42.5	-	106	0.55	-
5	22.5	-	-	43.7	-	105	0.56	-
7	21.4	-	-	44.3	-	106	0.48	-
9	23.4	-	-	-	-	106	0.50	-
11	24.6	1.6	7.6	45.4	88	106	0.49	32.9

5

First leach stage

The leach residue from the first leach stage simulation was filtered and washed with water and analysed. The results are shown in the table below.

10

Element	Unit	Zn Ferrite Feed	First Stage Leach Residue	First Stage Leach Extract.
Ag	ppm	444	15	97.6%
Cu	ppm	4960	2295	66.9%

Fe	%	22.2	27.5	11.3%
Pb	%	9.22	1.3	90.0%
Zn	%	15.0	14.6	30.6%
Mass	kg	**46.00**	**32.9**	

As can be seen from the table above, essentially all
of the silver and lead were extracted, while only 30% of

5   the zinc was extracted.

The leach residue from the first leach stage
simulation was then used as the feed to a second leach
stage simulation according to the process flowsheets
(Figures 1 and 2). The residue was slurried in 250 litres

10   of brine prepared according to the process flowsheet and
sulfuric acid was added over time. The results are shown
in the table below.

Time (Hours)	H₂SO₄ Addition (kg)	[Fe] (g/L)	[Cu] (g/L)	[Zn] (g/L)	Residue [Zn] (wt%)	Zn Cumul. Extraction (%)	[Ag] (ppm)	Temp	pH	Dry Weight (kg)
0	0	78	3.1	36	14.55	30.6	30	106	0	32.9
6	15	-	-	-	6.20	47.7	-	103	0	-
18		-	-	-	5.70	60.3	-	107	0	-
22	7.5	-	-	-	2.77	76.6	-	107	0	-
26		-	-	-	0.40	96.6	-	106	0	-
30	7.5	-	-	-	0.37	96.9	-	101	0	-
34		-	-	-	0.08	99.4	-	106	0	-
44		98	3.6	61	0.04	99.6	35	106	0	63.2

15

Second leach stage
A total of 30 kg of sulfuric acid was added over a period
of 44 hours and three separate doses equivalent to
addition rates of 330kg/t, 490kg/t and 650kg/t of zinc

24

ferrite residue (dry) were made. A small sample of the
leach residue was collected just before each acid addition
and analysed for zinc with the results shown in the table
below, along with the zinc extraction for the second leach
5   stage test, and the cumulative extraction for both first
and second leach stages.

H_2SO_4 Addition (kg/t)	Zn in Residue (wt %)	Extraction Leach 2 (%)	Cum. Extract. (%)
0	14.55%	0.0%	30.6%
330	5.70%	42.8%	60.3%
490	0.40%	95.4%	96.9%
650	0.12%	98.4%	99.6%

From these results it can be seen that high zinc
10   extraction can be achieved at an acid addition rate of 490
kg/t.

The whole of the leach residue from the second leach
stage test was filtered and washed with water, and then
analysed for a range of metals, with the results shown in
15   the table below (and including the first leach stage
results for clarity and comparison).

Element	Unit	Zn Ferrite Feed	First Stage Leach Residue	First Stage Leach Extract.	Second Stage Leach Residue	Second Stage Leach Extract.	Cumulative Extraction
Ag	ppm	444	15	97.6%	10	-28%	97%
Cu	ppm	4960	2295	66.9%	52.5	96%	99%
Fe	%	22.2	27.5	11.3%	2.15	85%	87%
Pb	%	9.22	1.3	90.0%	0.18	74%	97%

Zn	%	15.0	14.6	30.6%	0.12	98%	99.6%
Mass	kg	46.00	32.9		63.2		

From these results it can be seen that extraction
efficiencies for Ag, Cu, Pb and Zn are very high at 97% or
above, which clearly demonstrates the capability of the
5   process to treat zinc ferrite residues to recover metal
values.

Example 3

EAF Dust Leach Trials

10   A series of leach trials were carried out on a sample
of EAF dust. These types of materials were noted to be
mainly composed of refractory zinc ferrites along with
varying quantities of other more simple metal oxides
formed at high temperatures in the electric arc furnace.

15   First stage leach

The effectiveness of the first stage leach was tested by
preparing a slurry of 240 g of EAF dust in 4 litres of a
bromide-based brine with the following composition.

Component	Concentration (g/L)
$CaCl_2$	85
$CuCl_2$	40
$FeCl_3$	175
$PbCl_2$	10
$ZnCl_2$	170
NaBr	100

20

The solution metal concentrations were monitored over
time with the results shown in the table below.

Minutes	T (°C)	pH	Ag (ppm)	Cu (g/L)	Fe (g/L)	Pb (g/L)	Zn (g/L)	Dry wt (g)
0	90	< 0.1	< 0.1	20.3	56.7	7.0	79.7	240
10	91	< 0.1	-	-	-	-	-	-
30	94	< 0.1	2.1	20.2	50.3	7.0	97.6	-
60	97	< 0.1	2.2	19.9	49.2	7.7	97.1	-
90	97	< 0.1	-	19.9	49.1	7.6	97.4	-
120	93	< 0.1	2.3	19.9	49.0	6.7	97.4	-
150	94	< 0.1	2.4	19.9	49.1	6.0	95.1	-
180	96	< 0.1	2.2	20.2	49.7	6.0	-	180

The leach residue from the first stage leach
simulation was filtered and washed with water and analysed
5   with the results shown in the table below.

Metal	Unit	EAF dust feed	First Stage Leach Residue	First Stage Leach Extraction
Ag	ppm	45.5	0.9	98.5%
Cu	ppm	15150	1200	94.1%
Fe	%	20.55	39.0	-42.4%
Pb	%	2.81	4.2	-10.9%
Zn	%	30.6	6.8	83.3%
Mass	g	240	180	

The precipitation of iron into the leach residue was
the result of acid consumption from leaching of the EAF
10   dust. Essentially all of the silver and copper were
leached, along with 83% of the zinc. Some lead appeared
to precipitate from the solution, which may have resulted

from cooling of the solution during filtration. Due to the high recovery of the metals in the first stage leach, this residue did not need to be processed by a second stage leach.

5   The effectiveness of the first stage leach, for a system not containing bromide, was tested by preparing a slurry of EAF dust at a density of 100 g/L in a brine containing:

Component	Concentration (g/L)
$CaCl_2$	100
NaCl	50
$FeCl_3$	60

10

The leach residue from the first stage leach simulation was filtered and washed with water and analysed with the results shown in the table below:

Metal	Unit	EAF dust feed	First Stage Leach Residue	First Stage Leach Extraction
Ag	ppm	45.5	53	0
Cu	%	1.51	0.13	92.6
Fe	%	20.55	46.72	-95.4
Pb	%	2.81	0.31	90.6
Zn	%	30.6	8.06	77.4
Mass	g	20	17.19	

15

The residue was now used as a feed for a second stage leach test.

Second stage leach

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A second stage leach was conducted using the equivalent of 500 kg/t of H_2SO_4. The sulfuric acid was reacted with a brine of similar composition to that used in the first stage leach, yielding $CaSO_4.0.5H_2O$ and HCl.

5 The subsequent solution was added to the residue of the first stage leach.

The leach residue from the second stage leach simulation was filtered and washed with water and analysed with the results shown in the table below:

10

Metal	Unit	EAF dust feed	Second Stage Leach Residue	Second Stage Leach Extraction
Ag	ppm	45.5	9.2	88.2
Cu	%	1.51	0.12	95.4
Fe	%	20.55	46.4	-32.3
Pb	%	2.81	0.12	97.5
Zn	%	30.6	9.1	82.6
Mass	g	20.0	11.7	

Other studies of the second stage leach were conducted with brine containing only $CaCl_2$ at 165 g/L. Acidic brine was prepared by the addition of H_2SO_4

15 resulting in the precipitation of $CaSO_4$ and the generation of HCl. Slurries of EAF dust at a density of 100 g/L were prepared, and the equivalents of 200 kg/t and 550 kg/t of H_2SO_4 to feed were added to the slurries and reacted for 2 hours. The residues were filtered and

20 washed with water, and analysed with the results shown in the following table:

Metal	Unit	EAF dust feed	210 kg/t H_2SO_4		550 kg/t H_2SO_4	
			Residue	Extraction	Residue	Extraction
Ag	ppm	45.5	65	3.3	5	95.2
Cu	ppm	15150	2080	90.7	1800	94.9
Fe	%	20.55	28	7.8	46.1	2.8
Pb	%	2.81	3.53	15.9	0.83	87.3
Zn	%	30.6	22.9	49.3	15.6	77.9
Mass	g	30	20.31		13	

The differences between the metal concentrations in the two residues highlighted the sequential nature of the leach. Copper-bearing phases were leached with a small

5　amount of acid, while silver and lead were associated with the more refractory zinc phases, requiring much more acid for extraction. Greater extraction of the lead and zinc was expected given reaction times longer than 2 hours. Nevertheless, these results demonstrated the viability of

10　using a purely $CaCl_2$ brine in the second stage leach environment.

Example 4

Acid Generation Trials

15　The second stage leach required the addition of acid in the form of HCl. This was generated by the reaction of H_2SO_4 to a $CaCl_2$ rich brine as follows:

$$H_2SO_4 + CaCl_2 \rightarrow 2HCl + CaSO.xH_2O$$

20
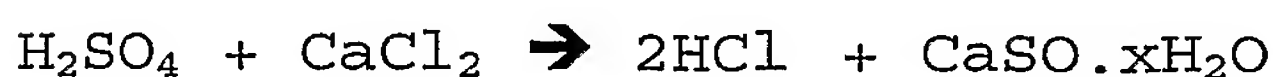
This example outlined the effect of temperature and brine composition on the water content and purity of the precipitate.

Brine containing only CaCl$_2$

Solutions containing 165 g/L CaCl$_2$ were heated to
50°C and 95°C. 10g of H$_2$SO$_4$ were added to the solutions and
mixed for 1 hour. The residues were filtered and washed
with water and ethanol and dried at 50°C. The analyses
were compared in the following table with the ideal
calcium and sulfur content of the minerals gypsum and
bassanite:

	Ca (%)	S (%)	Mineral
55 °C	23.01	18.42	Gypsum
95 °C	27.48	21.98	Bassanite
Gypsum	23.291	18.596	CaSO$_4$.2H$_2$O
Bassanite	27.626	22.057	CaSO$_4$.0.5H$_2$O

These results clearly demonstrated that the formation
temperature controlled the amount of crystalline water
present in the precipitate. X-ray diffraction data
confirmed the formation of these minerals.

Brine containing other metal halides beside CaCl$_2$

The generation of HCl was tested using a brine
obtained from the second stage leach of a nickel laterite
sample. 1 L of brine was heated to 100°C, 80g of H$_2$SO$_4$ was
added and the solutions mixed for 1 hour. The samples were
filtered and washed with water and ethanol, before drying
at 50°C. The chemical composition analysis is shown in
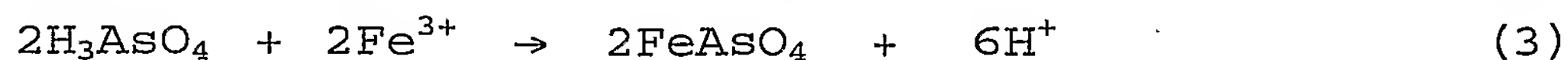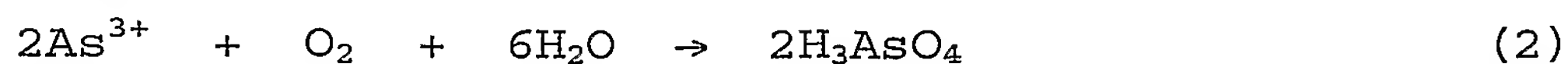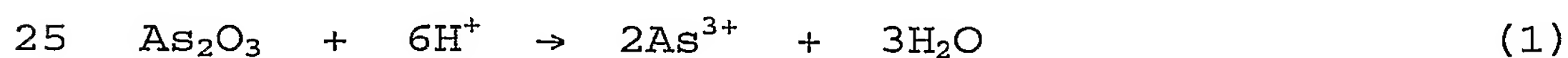the following table along with the initial brine
composition:

	Ca (g/L)	Co (g/L)	Fe (g/L)	Mg (g/L)	Mn (g/L)	Ni (g/L)		
Brine	50	2.7	35	30	17	14		

	Ca (%)	Co (ppm)	Fe (ppm)	Mg (%)	Mn (ppm)	Ni (ppm)	S (%)	Cl (ppm)
Residue	27.3	<0.1	0.07	<0.01	20	5	21.1	100

The high purity of the bassanite precipitate (as
confirmed by X-ray diffraction shown in Figure 3)
confirmed that the generation of HCl by the addition of

5   H_2SO_4 to a $CaCl_2$ rich solution occurred without loss of
metals to the precipitate. This was highly significant,
indicating that the precipitate could be sold or sent for
disposal without incurring penalties for metal impurities.
Furthermore, the water content of the mineral could be
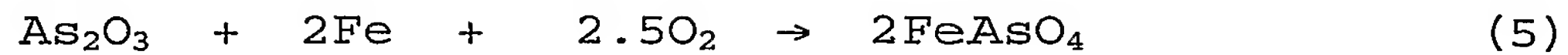
10 controlled by the temperature of the reaction.

Example 5

Arsenic trioxide from smelter and roaster waste
stockpiles was converted to a safe-to-dispose of ferric

15 arsenate using a first stage type leach similar to that
described in Examples 2 to 4.

A slurry containing the arsenic trioxide was prepared
in an acidified (HCl acid prepared as described in Example
4) chloride-based brine comprising dissolved ferrous ions

20 (eg. from a leachable source of iron, such as a laterite,
pyrrhotite etc). The slurry was agitated and sparged with
air for two hours at 90-95°C and a crystalline ferric
arsenate precipitate was recovered. The relevant equations
were:

25 $$As_2O_3 \; + \; 6H^+ \; \rightarrow \; 2As^{3+} \; + \; 3H_2O \tag{1}$$

$$2As^{3+} \; + \; O_2 \; + \; 6H_2O \; \rightarrow \; 2H_3AsO_4 \tag{2}$$

$$2H_3AsO_4 \; + \; 2Fe^{3+} \; \rightarrow \; 2FeAsO_4 \; + \; 6H^+ \tag{3}$$

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$$2Fe + 1.5O_2 + 6H^+ \rightarrow 2Fe^{3+} + 3H_2O \qquad (4)$$

$$As_2O_3 + 2Fe + 2.5O_2 \rightarrow 2FeAsO_4 \qquad (5)$$

Whilst a number of process embodiments have been described, it will be appreciated that the processes described herein can be embodied in many other forms.